COATINGS AND ENAMELS

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EFFECT OF SEMICONDUCTING TITANIUM DIOXIDE ON THE RESISTIVITY OF A COMPOSITE GLASS ENAMEL COATING

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It is shown that the electric conductivity of TiO_2 (rutile) can be increased by doping it with oxides of elements possessing higher valence. Adding semiconducting TiO_2 to glass enamel slip makes it possible to decrease the resistivity of a composite coating considerably.

Key words: glass enamel, composite coating, slip, electric conductivity, titanium dioxide.

Glass enamel coatings used for corrosion protection of chemical apparatus and pipes are good dielectrics with resistivity exceeding $10^{12}\ \Omega \cdot$ cm and prevent the leakage of static electricity from the working surfaces of apparatus used for reprocessing electrically insulating materials. On the basis of the rules for protection from static electricity [1] the resistivity of a glass enamel coating on apparatus operating under dangerously explosive conditions should be at least $10^8\ \Omega \cdot$ cm.

One way to lower the resistivity of glass enamel coatings could be to create compositions by chemically introducing current-conducting fillers into the glass enamel mix.

Analysis of the published data on the effect of various fillers on the physical – chemical and technological properties of silicate enamels shows that titanium or tin dioxides could be most suitable for such purposes, TiO_2, which is distinguished by a high CLTE and resistance to mineral acids and low density, being preferable.

Titanium dioxide with stoichiometric composition is characterized by a quite high resistivity — higher than $10^{11}\ \Omega \cdot$ cm [2]. The specific volume resistivity of TiO_2 decreases considerably when this compound is partially reduced and trivalent titanium ions Ti^{3+} are formed or when it is doped with ions of higher valence, for example, Nb^{5+} or Ta^{5+} [3]. Nb^{5+} with radius 0.66 nm, close to the radius of tetravalent titanium, become embedded in the rutile lattice, replacing the Ti^{4+} ions forming at the same time a weakly bound electron, which is what produces the higher resistivity of rutile.

The objective of the present work is to study the effect of semiconducting TiO_2 on the resistivity and certain technological properties of composite glass enamel coating.

Commercially pure R-02 (rutile form) TiO_2 was used. The resistivity of TiO_2 — initial and doped with oxides of the type R_2O_5 (RO_3) — was measured for 18 mm in diameter and 4 – 5 mm high tablets pressed from carefully premixed powders under pressure 80 MPa and heat-treated at 1300°C for 4 h.

To measure the resistivity of the composite material the pellets were pressed from powders consisting of TiO_2 (filler) and a glass matrix — commercial corrosion-resistance glass enamel 54l [4] (the total content of the filler and glass matrix was 100%). The tablets were heat-treated at 830°C for 10 and 30 min. The resistivity was measured with an E6-10 ohmmeter on ground samples with graphite electrodes.

The slip for the composite covering enamel was prepared in a ball mill by combined grinding of TiO_2 powder and glass matrix with clay, water, and electrolytes added. The prepared mix was deposited on 60 × 40 × 10 mm steel samples which were primed with 482 semiconducting primer (USSR Inventor's Certificate No. 590940). The covering enamel was fired at 830°C for 10 min. The thickness of the coating was determined with an MIP-10 magnetic thickness meter, and the LTEC and softening onset temperature of the composite material were determined with a DKV-4 dilatometer using samples cast from slip in a paper mold, dried, and heat-treated at 830°C in 10 min.

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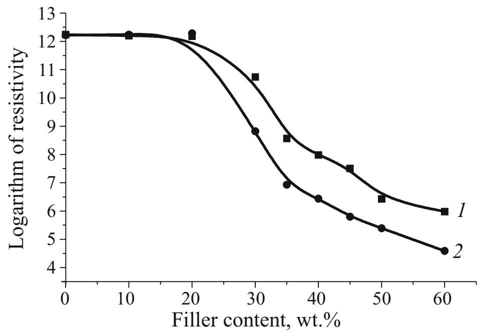

Fig. 1. Effect of semiconducting TiO_2 on the volume resistivity of composite material heat-treated at 830°C for 10 min (*1*) and 30 min (*2*).

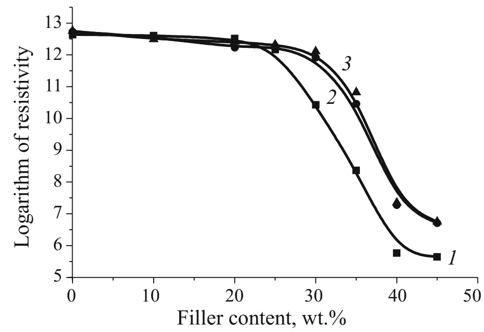

Fig. 2. Volume resistivity of a composite coating versus the content of the semiconducting titanium dioxide. The numbers on the curves correspond to the number of coating layers.

Effect of R_2O_5 (RO_3) Oxide Additives on TiO_2 Resistivity

Dopant molar content 0.5%	Rutile volume resistivity at 100°C, $\Omega \cdot$ cm
No additives	4.32×10^{12}
Nb_2O_5	1.32×10^6
Sb_2O_5	4.00×10^6
Ta_2O_5	6.32×10^5
MoO_3	1.14×10^9
WO_3	2.25×10^5

It is evident that small additions of oxides (0.5% molar content) decrease the resistivity of rutile considerably.

TiO_2 with 2% (molar content) Nb_2O_5 was used subsequently. Titanium and niobium oxide powders were mixed and fired in a gas furnace at 1300°C for 4 h. The resistivity of the sinter obtained was $3.6 \times 10^3 - 1.3 \times 10^7\ \Omega \cdot$ cm. The introduction of semiconducting TiO_2 into the glass matrix in amounts 20%[2] and less has virtually no effect on the resistivity of the composite material (Fig. 1). A substantial decrease of the resistivity of the composite glass matrix – filler is observed for TiO_2 content 30% and higher. Increasing the heat-treatment time of the composite from 10 to 30 min decreases the resistivity with filler content above 30% considerably.

A similar dependence of the resistivity on the filler content was also observed on the coating. For a low filler content (10 – 20%) the resistance of the coating remains practically unchanged and is higher than $10^{12}\ \Omega \cdot$ cm (Fig. 2). For filler content above 20% the resistivity of the coating decreases to $10^5 - 10^6\ \Omega \cdot$ cm (Fig. 2). As more layers are deposited, the resistivity of the coating decreases with higher filler content. It should be noted that as the TiO_2 content increases above 20% the firing interval of the coating shifts to higher temperature 860 – 880°C.

The semiconducting TiO_2 powder introduced into the 54l enamel slip increases the heat-resistance of the coating from 220°C for the initial 54l enamel to 280°C for 40% TiO_2 content. The CLTE decreases from 105.3×10^{-7} to $98.7 \times 10^{-7}\ K^{-1}$. The acid resistance of the coating (mass loss in 20% boiling hydrochloric acid) decreases from 0.087 mg/cm^2 for enamel 54l to 0.223 mg/cm^2 for a coating containing 40% TiO_2.

The following feature of the composite coatings obtained should be noted. The resistivity of the coatings containing 30% or more of semiconducting TiO_2 decreases considerably (by 2 – 3 orders of magnitude) and remains small after a high voltage is applied to the sample, for example, after treatment with an IDC-02 indicator of continuity defects at voltage 2 kV and higher. This could be due to the fact that when the content of the filler is about 30% individual TiO_2 particles are insulated from one another by thin films of the glass matrix, and a high voltage applied to the coating causes electric breakdown of these films and increases the electric conductivity. For filler content 35% and higher, current-conducting chains of semiconducting TiO_2 start to form and high voltage, breaking through the insulation films around individual TiO_2 particles, together with the chains form additional conducting structures. This feature is of practical interest because the required electric conductivity can be obtained with a lower content of the semiconducting fill by applying a high "forming voltage" to a coating for a short time.

In summary, the electric conductivity of TiO_2 (rutile) can be increased by doping it with oxides of elements whose valence is higher. Introducing semiconducting TiO_2 into the glass enamel mix decreases the resistivity of the composite coating considerably.

[2] Here and below — content by weight.

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